Colloids and Colloidal Electrolytes.

By Prof. J. W. McBain.

COLLOIDS comprise all matter that is made up of particles smaller than a wave-length of light, but larger than a single molecule of an ordinary crystalloidal substance such as sugar, salt, or water. It would appear that in some cases the chemical molecules are linked together into particles of colloidal dimensions, and then from these particles are built up the familiar structures such as rubber, fibres of cotton, wood, or earthenware. It is a moot question as to whether, in the case of certain highly complex organic substances, the single molecules themselves may not be large enough to exhibit the distinctive properties of colloidal particles.

Scientific study has been devoted almost exclusively to mixtures in which colloidal particles are dispersed throughout a second continuous medium; such as in many precious stones, ink, the body fluids, or a bar of soap where the continuous medium is water. Furthermore, the investigations of physical chemists have been directed almost entirely to the study of very dilute colloidal solutions (sols) such as dilute suspensions of gold or arsenic trisulphide in water, whilst biologists have devoted a great deal of attention to gelatin and protein, colloids of a very different type. For this reason the innumerable observations that have been made on colloids have not been well linked up either with each other or with our general scientific knowledge. There are, however, two outstanding instances in which some of the familiar and unambiguous methods of classical physical chemistry have been extended to the study of highly characteristic colloids—namely, soaps, chiefly studied in this country, and proteins, chiefly elucidated by W. B. Hardy and by the professor of biophysical chemistry in Vienna University, Wolfgang Pauli.[1] It now appears that soaps, proteins, and gelatin salts are closely similar types of substances, whilst soaps are by far the most accessible to quantitative measurements.

A very important characteristic of most colloidal solutions which have received careful study is the fact that the colloidal particles possess electrical charges. For instance, silver particles of diameter of about 500 millionths of a millimetre, suspended in water, move under the influence of an electric field. This must be ascribed to electrical charges on the particles, and calculation shows that on each such particle there are anything up to 100 million negative charges or electrons. This electrical charge seems enormous until we reflect that it is relatively ever so much less than the number of atoms of silver, and that in an ordinary ion there is one electrical charge for each atom.

The stability of the dilute suspensions of such insoluble substances greatly depends upon these electrical charges.

As will be shown, these "irreversible" or "suspensoid" particles, which have been so largely studied, occupy an intermediate position between electrically neutral colloidal particles, such as rubber in solution in benzene, and the much more highly charged colloidal particles known as the ionic micelle that occur in such aqueous solutions as those of soap. In the ionic micelle or particle the number of electrical charges is commensurate with the number of molecules or ions which have aggregated together.

Another prominent characteristic which physical chemists have met in attempting to study suspensoid colloids is their extreme variability and sensitiveness to all sorts of disturbing influences. It has become almost an axiom that only variable and non-reproducible results can be expected, and that they depend on the individual specimen examined. It is all the more fortunate, then, that in the case of soap solutions it is possible to obtain quantitative reproducible results depending only upon the composition and the state of the system. This has enabled us to investigate through these comparatively simple substances of known molecular formulæ and structure some of the characteristic properties exhibited by solutions of so many of those extraordinarily complex chemical substances, mostly of unknown formulæ, which are involved in all life processes, and are frequently of very great industrial importance. Salmon's suggestion is that these colloids should be called "equilibrium colloids," a classification that would in practice more or less correspond to the present modified use of Hardy's term "reversible colloids," now used chiefly with reference to the properties of dried residues. The expression "equilibrium colloids" has the advantage of possessing a rather deeper significance.

In the study of soap solutions in the Bristol University laboratory, it was first established that they exhibited excellent electrical conductivity even in the most concentrated viscous solutions. The change in conductivity with concentration exhibited remarkable anomalies such as had hitherto been met with only in certain non-aqueous solutions. The curve passes through both a maximum and a minimum in moderately strong solution. At this time it had been generally considered that colloids as such could not exhibit conductivity, and if observed it was ascribed to impurities and admixtures.

Although there were no admixtures in the case of these specially pure soap solutions, no data at all existed with regard to the amount of alkali set free in the solution through hydrolysis of the soap by the solvent water. Direct measurements succeeded in showing through two independent methods, electromotive force and rate of catalysis, that the hydrolytic alkalinity of soap solutions is for most purposes negligible, and hence that the conductivity observed must be proper to the soap itself. Incidentally, this result is of interest in showing that the process of saponification in the manufacture of soap could be much more complete than was thought by such authorities as Lewkowitsch.

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[1] A comprehensive summary of Pauli's masterly researches on this particularly complicated material is to be found in his "Kolloid-chemie der Eiweisskörper." Pp. 109. (Dresden and Leipzig: Th. Steinkoph, 1920.)

A further essential stage in the development of this problem was attained through the study of the osmotic activity of the soap solutions. This property is, in such cases, surprisingly inaccessible to trustworthy quantitative measurement. However, a development of Cumming's dew-point apparatus gave a general method of securing data, and the results were confirmed by cryoscopic measurements upon the few soaps which could be studied in solution at 0°. The upshot is that a mass of trustworthy data proves that soaps exhibit osmotic activity comparable with that of an ordinary crystalloid such as sugar.

This at once exposed a fundamental difficulty in interpreting the results according to any of the other hitherto recognised theories of physical chemistry. The conductivity is that of a highly dissociated salt, whereas the osmotic activity is scarcely equal to that of an undissociated crystalloid, and yet many years of work had been devoted to establishing the trustworthiness of each of these facts. Examination of the results of the concentrated solutions of the higher soaps showed that, whereas the conductivity corresponded to that of two good conducting ions, the osmotic pressure was only that of one ion altogether. In other words, the osmotic result proved that the only crystalloidal constituent of such a solution was the sodium or potassium ion, all the other constituents, including whatever accounted for quite half the conductivity, being colloidal.

Hence we are driven to the conclusion that there are present in these solutions colloidal particles, the "ionic micelle," possessing an actual conductivity often several times greater than that of the sum-total of the ions which are contained in it, and which in so aggregating have retained their electrical charges. These aggregates are so large that they have little or no osmotic effect. For suggestions that make plausible the properties and stability of such aggregates, reference must be made to papers published by the Royal Society and the London and American Chemical Societies, where also it is shown how these conceptions explain the various properties of soap solutions. Direct measurements are now being carried out to test even more directly the validity of the explanations here advanced.

For the sake of clearness it should be emphasised that conductivity is not identical with rate of movement in an electric field, for it is a remarkable fact that matter in all states of subdivision from single atomic ions up to coarse granules may move at roughly the same rate in an electric field. This movement (cataphoresis) in the case of a fine grain of sand might thus be equal in magnitude to that of one of the slower ions, whereas the resulting equivalent conductivity is only infinitesimal. The ionic micelle of soap solutions is noteworthy in that its mobility in an electrical field exceeds that of most true ions.

It is probable that quite general laws underlie the behaviour of colloidal particles together with all surfaces of separation in which ionising solvents are involved, thus including emulsions as well as large continuous surfaces.

In another respect, too, soap solutions afford a particularly good example for the study of a colloid in that the whole gamut of transition stages between ordinary salts and colloids can be illustrated by choosing the salts of the various fatty acids, or even by a mere change in concentration of a solution of any one of these. In dilute solution the soaps are largely present as simple salts, whereas in concentrated solutions of the higher soaps we have the complete formation of colloidal electrolyte.

Having gained some insight into the properties and behaviour of the slightly charged colloids and the highly charged colloidal electrolytes, the greatest need at the present time for the development of colloid chemistry is the discovery of some method of studying neutral uncharged colloids, such as, for instance, rubber or nitrocellulose solutions. No one has yet succeeded in developing a general method for obtaining quantitative data of direct significance, and a big advance is to be hoped for in this direction. This would probably lead to rational methods for the study of such familiar but complicated structures as the textiles, or paper, in which solvent is no longer present.

Recent study of soap solutions in the Bristol University laboratory has shown, further, that they can exist in three distinct characteristic forms—namely, clear, somewhat viscous, liquid sols, transparent elastic gels, and white opaque curds. Nearly all our previous knowledge of the properties of jellies has been due to the study of gelatin, usually containing admixed and partly combined salts or acids. The simpler case of the soap gels is, again, suited for study because no extraneous substances are present, and, as we have seen, the various constituents of the soap solution are characterised by well-marked properties such as conductivity and osmotic activity.

It has now been shown that the properties of soap solutions are independent of whether the solution is in the form of sol or gel except for the distinctive mechanical properties of the latter. In other words, the chemical equilibria, and hence the colloidal particles, are identical in sol and gel. This means that the gel structure must be built up of the same colloidal particles as were present in the sol. The possibilities as to the nature of this structure are severely limited by the fact that the conductivity remains unaltered. Hence we must infer that the colloidal particles are stuck together to form loose aggregates, which may be fragments of irregular network, or more probably innumerable filaments, which, being embedded in the solution, give to the whole its temporary rigidity and elasticity. Many other lines of evidence support this view. For instance, the optical evidence shows that the structural elements in the gel are of very fine colloidal dimensions, far below the powers of the microscope. This conclusion that the particles in sol and gel are identical in number and nature shows that nothing analogous to crystallisation has taken place.

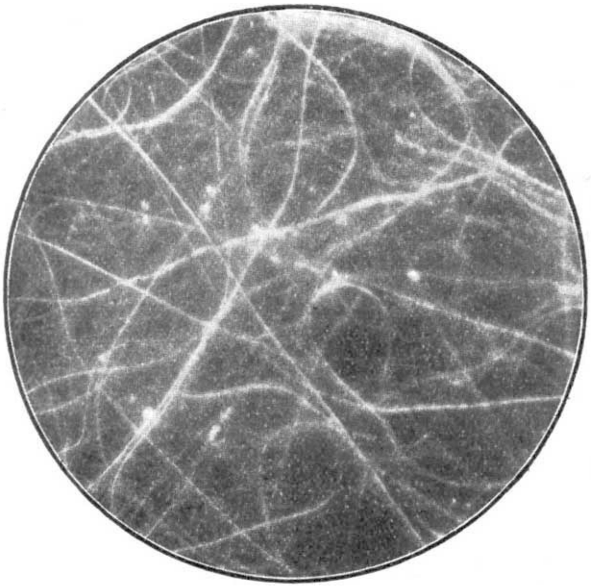

FIG. 1.—Ultramicroscopic appearance of a sodium soap (0·8*N* Sod. Myristate, × 600).

In clear contradistinction to this, curds and coagula are formed by a process closely analogous to crystallisation. Soap sols and gels show almost nothing in the ultramicroscope with its dark ground illumination, but when solidification to white curd begins white fibres of barely microscopic diameter are seen to shoot out until the whole becomes a dazzling white felt of these fine fibres. Fig. 1 (magnification 600) illustrates this appearance in a typical sodium soap, the myristate, in this its permanent stable state. To the naked eye it appears as a hard white cake of soap. Fig. 2, the stearate, exemplifies the more complicated behaviour of soft potassium soaps, in which the fibres that first appear are extremely short, and often twinned, but in which, on standing, true microscopic crystalline plates appear. These tiny crystals undoubtedly account for the "figging" which is seen in most good soft soaps.

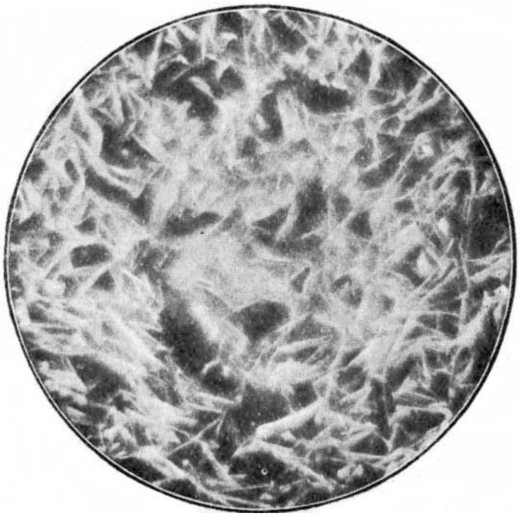

FIG. 2.—Ultramicroscopic appearance of a potassium soap (0·5*N* Pot. Stearate, × 500).

Work at the Bristol University laboratory has not been confined to the elucidation of the results here outlined, but an extensive programme of investigation of the colloid and phase-rule phenomena involved in the typical processes of soap boiling is in progress, in the expectation that the precise elucidation of the behaviour of this particularly suitable and characteristic material may lead to the better understanding of some of the typical problems of the physical chemistry of the colloidal state.

Inland Waterways.[1]

By DR. BRYSSON CUNNINGHAM.

THE outstanding feature of Mr. Minikin's book is the very interesting series of photographic illustrations which it contains; these impart a most effective realisation of the physical characteristics of the watercourses described in the text. They are a most serviceable adjunct, and some of the views have the additional charm of being picturesque. We reproduce two by way of example.

The work consists of ten chapters, of which the first is preliminary, and the second deals with general considerations relating to torrential phenomena, bends, valleys, and erosion, while chap. iii. is on rainfall. The available rainfall, or run-off, is said to vary between 20 per cent. on permeable soils and 75 per cent. on impermeable ground. As limits, these are perhaps somewhat wide, and might, in this country at any rate, be appreciably narrowed. From a survey of flood discharges in England and Wales it has been computed by Mr. Clayton that in average areas the run-off to the sea is between 50 and 60 per cent. of the total rainfall. Transpiration, as a source of absorption of rainfall, receives little notice. Chap. iv. deals with river surveys, and in particular describes methods applicable to running

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[1] "Practical River and Canal Engineering." By R. C. Royal Minikin. Pp. vii+123+12 plates. (London: Charles Griffin and Co., Ltd., 1920.) 12*s*. 6*d*.